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12b. DISTRIBUTION CODE**13. ABSTRACT (Maximum 200 words)**

We have devised an iterative convergent/divergent approach to conjugated oligomers that might serve as molecular wires. The molecular length doubles with each iteration. The systems prepared are completely monodispersed and based upon oligo(thiophene-ethynylene)s (1) and oligo(phenylene-ethynylene)s at 100 Å and 128 Å long, respectively. The optical and SEC properties will be discussed. Methods are outlined to attach end groups that might serve as molecular alligator clips.

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Technical Report No. 37

Potential Molecular Wires by an Iterative Divergent/Convergent Approach. Doubling of Molecular Length at Each Iteration.

by

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Potential Molecular Wires by an Iterative Divergent/Convergent Approach. Doubling of Molecular Length at Each Iteration.

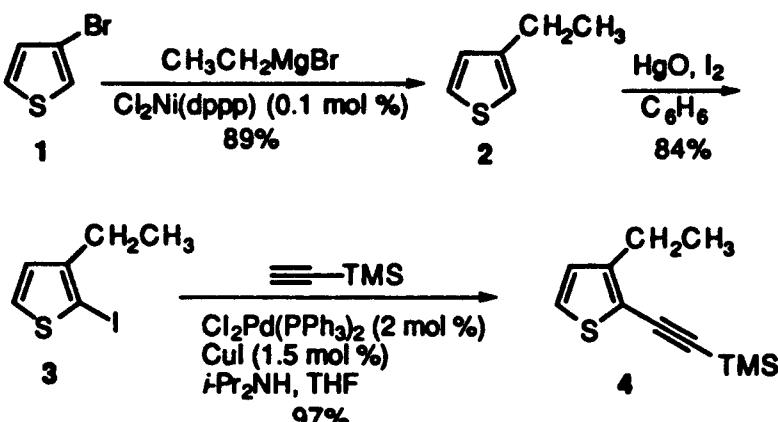
Darren L. Pearson, Jeffry S. Schumm, LeRoy Jones II, and James M. Tour*

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The ultimate computational system would consist of logic devices that are ultra dense, ultra fast, and molecular-sized.¹ We recently described the synthesis of two orthogonally fused conducting oligomers that may possess device functions.² However, before we can address the device-like properties, there is a more fundamental question; namely, can a single organic molecule even conduct electricity?³ Though bulk organic materials can indeed be semiconducting or even conducting,⁴ electronic conduction based upon single or small packets of molecules has not been demonstrated and it is theoretically controversial.^{1,5} Present nanopatterning techniques allow lithographic probe assemblies to be engineered down to the 100 Å gap regime.⁶ In an attempt to span this 100 Å gap with molecules and to assess the feasibility of molecular wire conduction, we describe here a new rapid synthetic approach to potential molecular wires based on oligo(thiophene-ethynylene) and oligo(phenylene-ethynylene) derivatives.

Others have constructed well-defined homogeneous conjugated oligomers up to 75 Å long.³ Our approach to such compounds is different in that it maintains several key features that make it well-suited for the requisite molecular frameworks for molecular electronics study. Specifically, our route involves (1) a novel rapid construction method that permits doubling molecular length at each coupling stage to rapidly afford a 100 Å and 128 Å oligomer, (2) an iterative approach so that the same high yielding reactions can be used throughout the sequence, (3) the synthesis of conjugated compounds that are known to be semiconducting in the bulk,⁷ (4) products that are stable to light and air so that subsequent engineering manipulations will not be impeded, (5) products that could easily permit independent functionalization of the ends to serve as "molecular alligator clips" that might be required for surface contacts to metal probes (for example, an end group containing a thiol would bond to a gold surface)⁸ (6) products that are rigid in their frameworks so as to minimize conformational flexibility yet containing substituents for maintaining solubility and processability, and finally, (7) products that serve as useful models for the understanding of bulk polymeric materials.⁹

The synthesis of the key monomer **4**, whose length will double at each stage, is below.¹⁰ The iterative divergent/convergent

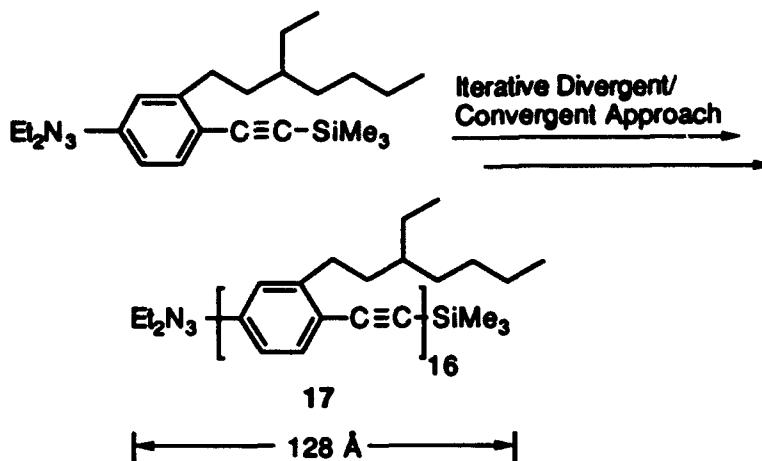


synthetic approach is outlined in Scheme I. The sequence involves partitioning **4** into two portions; iodinating the 5-position in one of the portions to form **5** and protodesilylating the alkynyl end of the second portion to form **6**. Bringing the two portions back together in the presence of a Pd/Cu catalyst^{10c-f} couples the aryl iodide to the terminal alkyne, thus generating the dimer **7**. Iteration of this reaction sequence doubles the length of the dimer **7** to afford the tetramer **10**, and so on to the octamer **13**, and finally the 16-mer **16**.

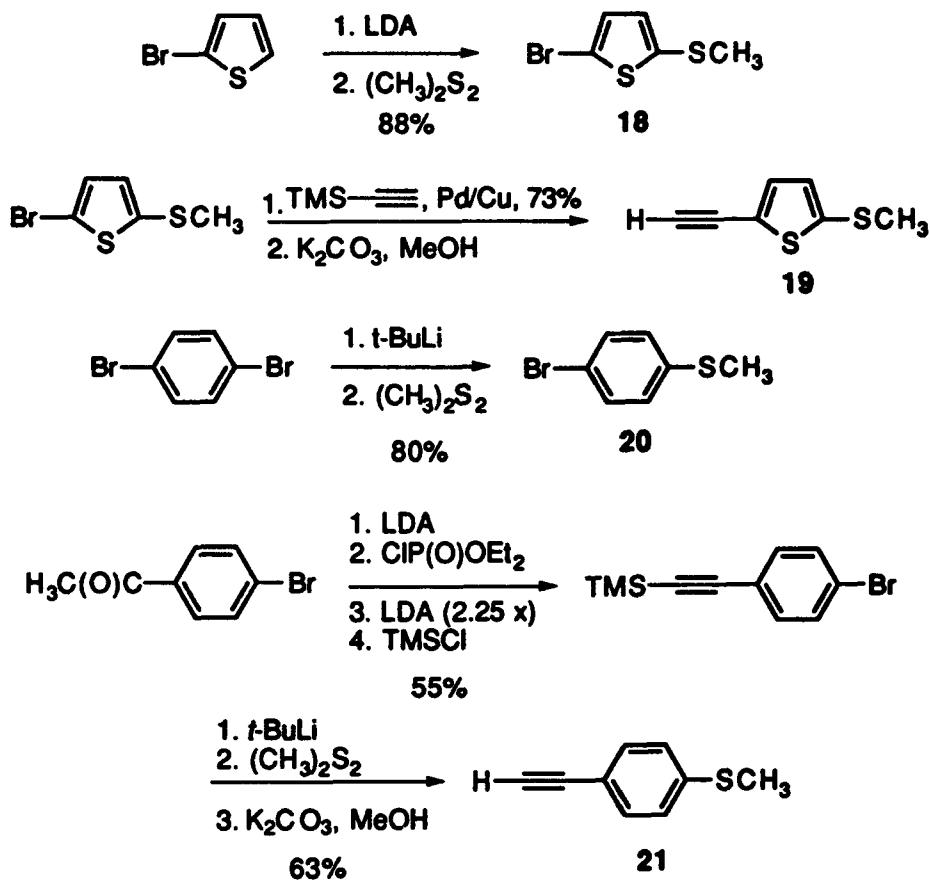
The monomer through 16-mer, **4**, **7**, **10**, **13**, and **16**, have been fully characterized. In every case, they are of $\geq 97\%$ purity. While the monomer through octamer afforded molecular ions by direct exposure via electron impact mass spectrometry (MS), neither this method nor FAB or electrospray MS sufficed for obtaining a molecular ion of **16**. However, matrix assisted laser desorption MS did afford an $M+1$ peak for **16** [Calc'd M (isotopic maximum with two ^{13}C) + 1 = 2221.37. Found peak maximum = 2219.98 ± 1.20].

The optical spectra are interesting in that a near saturation of the systems appears to have occurred by the octamer stage so that doubling the conjugation length to the 16-mer caused little change in the absorbance maximum. The results of the size exclusion chromatography (SEC) are also quite intriguing. SEC is not a direct measure of molecular weight but a measure of the hydrodynamic volume. Thus, by SEC using randomly coiled polystyrene standards, the number average molecular weights (M_n) of rigid rod polymers are usually greatly inflated relative to the actual molecular weights (MW). Accordingly, the SEC recorded M_n values of the octamer (**13**) ($M_n = 1610$, actual MW = 1146) and 16-mer (**16**) ($M_n = 3960$, actual MW = 2220) were much greater than the actual MWs. Conversely, the monomer (**4**) through tetramer (**10**) had M_n values that were very close to the actual because they are in the low MW region, prior to significant polystyrene coiling. In all cases, the SEC-determined values of $M_w/M_n = 1.02-1.05$ were within the detectable range limits.

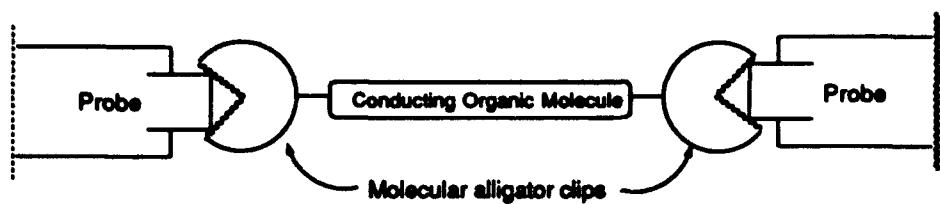
We have recently synthesized an analogous oligo(phenyleneethynylene) (**17**) by a similar route.



We have also synthesized a series of end groups (18-21) that will serve as molecular alligator clips. These end groups, upon



demethylation to the free thiols, will attach the ends of the molecules between the gold-coated probe surfaces as shown on Figure 1.



In summary, we have demonstrated the utility of this iterative divergent/convergent approach to the synthesis of very large molecular frameworks. We are presently synthesizing near-sp²-orbital matched arrays involving oligo(thiophene-ethenylene)s and oligo(phenylene-ethenylene)s.

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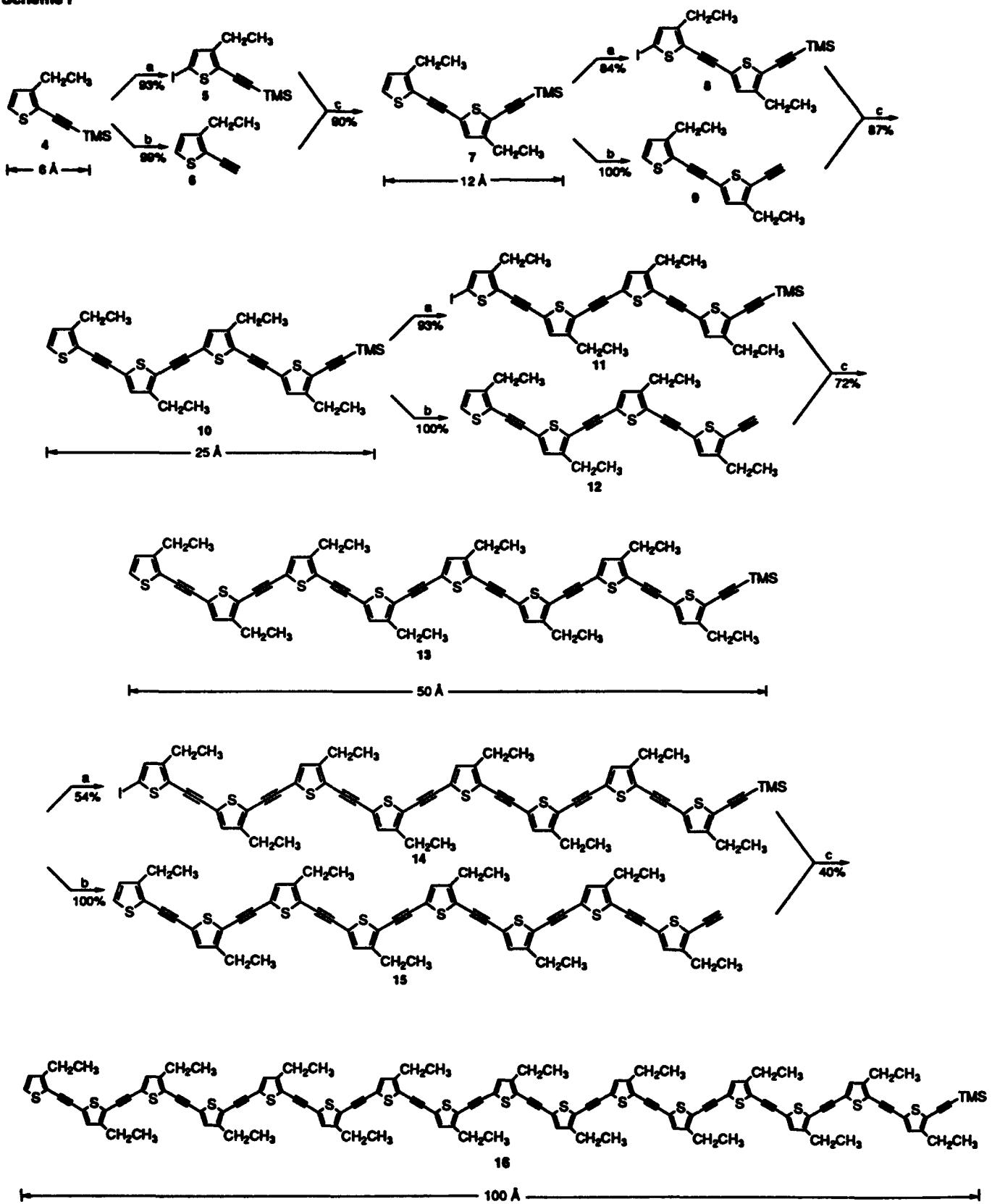
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Scheme I



Reagents: (a) LDA, Et_2O , -78° to 0°C then I_2 , -78° . (b) K_2CO_3 , MeOH , 23°C . (c) $\text{Cl}_2\text{Pd}(\text{PPh}_3)_2$ (2 mol %), CuI (1.5 mol %), THF , $i\text{-Pr}_2\text{NH}$, 23°C .